

# GRAVITATIONAL EFFECTS ON DISTORTION IN SINTERING

Randall M. German

Brush Chair Professor in Materials, Center for Innovative Sintered Products  
P/M Lab, 147 Research Building West, Pennsylvania State University, University Park, PA 16802-6809

## Abstract

During sintering a powder compact gains strength through low-temperature interparticle bonding, usually induced by solid-state surface diffusion, followed by further strength contributions from high-temperature densification. In cases where a liquid phase forms, sintering densification is accelerated and shape retention is sustained while open pores remain and contribute capillary forces. Unfortunately, sintering densification requires the compact become thermally softened to a point where creep strain rates reach levels near  $10^{-2} \text{ s}^{-1}$  when the liquid forms. On the other hand, thermal softening of the powder compact substantially reduces the strength at high temperatures. Therefore, the *in situ* strength evolution during sintering is a primary focus to separate compact densification (as required for high performance) with minimized distortion (as required for net-shaping). With respect to gravitation effects on distortion during sintering there are two points of substantial weakness - prior to significant interparticle bonding and during final pore closure. This research is focused on understanding the competition among interparticle neck growth, densification, thermal softening, grain boundary wetting, capillary effects associated with liquid wetting and residual porosity, and gravity. Most surprising is the apparent role of gravity, where the deviatoric stress acting on the powder structure induces skeletal formation that reduces distortion. In contrast with theory, microgravity samples exhibit more distortion yet fail to fully densify.

Results are presented on the experimental concepts supporting an emerging model of sintering strength evolution that enables understanding of both distortion and densification. The experiments have relied on tungsten heavy alloys, various combinations of dihedral angle, pore size, initial porosity, liquid:solid ratio, and heating rates. On Earth, the dominant factor with respect to distortion is the starting body heterogeneity. Current modeling efforts are seeking some means to uniformly predict the distortion based on a starting pore structure heterogeneity parameter. Densification is largely unaffected by the initial pore structure, but distortion is highly variable, suggesting that nonuniform pore closure might be a significant parameter during sintering. With respect to flight experiments, plans include removal of the solid body forces acting on the solid grains, allowing stabilization of the pore structure and examination of the buoyancy effects with regard to distortion. In microgravity there is the surprising result that compacts do not densify, yet distort – a factor that is contrary to all current sintering models.

Densification without distortion during liquid phase sintering was achieved by manipulating microstructure and its evolution during sintering. Microstructure parameters such as the solid volume fraction, dihedral angle, initial porosity, and pore size were varied to measure densification and distortion behavior during LPS using W-Ni-Cu alloys. Green compacts were formed using ethylene-bis-stearamide as a pore-forming agent with the amount of polymer controlling the initial porosity. Different initial pore sizes were

---

## Keywords: flight

\*Corresponding author. email: [rmg4@psu.edu](mailto:rmg4@psu.edu)

generated by varying the polymer particle size. Dihedral angle was varied by changing the Ni:Cu ratio in the alloys. Finally, the solid volume fraction was adjusted via the tungsten content. Distortion was quantified using profiles determined with a coordinate measuring machine to calculate a distortion parameter. Sintering results showed that solid volume fraction and dihedral angle are the dominant factors on densification and distortion during liquid phase sintering. Distortion decreases with increasing solid volume fraction and dihedral angle, while initial porosity and pore size have no observable effect on distortion at nearly full densification. Various strategies emerge to improve distortion control in liquid phase sintering.

## **Introduction**

Liquid phase sintering is broadly used for net-shape manufacturing [1, 2]. In many systems the liquid enhances densification, since it provides a capillary force that pulls the solid grains together and offers a fast mass transport medium [3, 4]. However, liquid phase sintering is generally limited to high solid content compositions due to shape retention difficulties. In tungsten heavy alloys, the large density difference (over 10 g/cm<sup>3</sup>) between tungsten grains and the matrix (usually Ni, Cu, or Fe) induces tungsten grain settling along the gravitational direction, especially for liquid contents over approximately 25 vol.%, resulting in significant distortion [5, 6].

Densification has long been the subject of many investigations, and distortion has also been studied in recent works [5, 6, 7], but few reports have directly addressed distortion control. A systematic investigation of distortion is lacking. Similarly, the initial pore structure effects on distortion have been neglected and are still uncertain at this time. This work studies liquid phase sintering by investigating the microstructural effects on the combination of densification and distortion, including solid volume fraction, dihedral angle, green porosity, and green pore size. In this work, W-Ni-Cu tungsten heavy alloys with varying dihedral angles were liquid phase sintered and simultaneously monitored for densification and distortion. The sequence of densification and distortion during liquid phase sintering was investigated using quenching experiments. Processing strategies brought forth by this research aid in liquid phase sintering practice for the fabrication of high density and high precision components.

## **Experimental Procedures**

The W-Ni-Cu tungsten heavy alloys with varying microstructures were fabricated from mixed powders. To control the green porosity and pore size, an organic binder, EBS (ethylene-bis-stearamide) was added to the powder mixture. During heating, the binder decomposed to leave pores in proportion to added concentration. Varying binder particle sizes created different green pore sizes. Dihedral angles were varied through the Ni:Cu ratio from 8:2 to 2:8. The initial formulations were adjusted to give final solid volume fraction (pore-free) ranging from about 60 to 85 vol.% using initial tungsten contents and the alloy balance being Ni and Cu.

The as-received tungsten powder was first deagglomerated by rod milling for 1 h in a 2000 cm<sup>3</sup> plastic jar filled with argon. The ratio of rods to the powder was 10:1. The W, Ni, and Cu elemental powders were first mixed according to the target composition, and then mixed with the EBS binder at different particle sizes in a Turbala mixer for 20 min to achieve a homogenous distribution. The binder content in the mixture was in proportion to the desired green porosity.

The mixed powders were weighed and uniaxially die pressed at 175 MPa into cylinders 12.8 mm in diameter and 10 mm in height. The green compacts were heated to extract the binder at 550°C for 1 h in

dry hydrogen with dew point of  $-55^{\circ}\text{C}$ . The hydrogen flow rate was 23 turnovers/h, and the heating rate was  $3^{\circ}\text{C}/\text{min}$ . After the binder was extracted, the compacts were weighed and measured again to calculate the green porosity.

Sintering was performed at  $1480^{\circ}\text{C}$  in a CM horizontal tube furnace in dry hydrogen with dew point of  $-55^{\circ}\text{C}$ . The hydrogen flow rate was 35 turnovers/h. The heating rate was  $10^{\circ}\text{C}/\text{min}$ , and the holding time at sintering temperature was 30 min. To reduce oxidation, a 30 min hold at  $1050^{\circ}\text{C}$  was employed during heating.

Quenching experiments were employed to investigate the sequence of densification and distortion during liquid phase sintering. The 80W-16Ni-4Cu compacts with 67% green porosity were sintered at  $1480^{\circ}\text{C}$  in a CM vertical furnace in dry hydrogen atmosphere with dew point of  $-55^{\circ}\text{C}$ . The hydrogen flow rate was 24 turnovers/h, heating rate was  $10^{\circ}\text{C}/\text{min}$ , and sintering holding times were from 0 to 30 min. After the sintering temperature and holding time were achieved, the samples were quenched into water at room temperature.

After sintering, distortion was quantified using a distortion parameter. Compact dimensions were first measured at various heights using a coordinate measuring machine (CMM). The measured sectional radii were normalized with respect to the maximum radius of the sintered compact. The distortion parameter equals the standard deviation of the normalized radii.

The densities of the sintered compacts were measured using water immersion method. Prior to measurement, the samples were infiltrated with light paraffin oil in a vacuum chamber for 15 min to fill all open pores.

Finally, the samples were sectioned along the longitudinal direction, mounted, and polished to a  $0.05\ \mu\text{m}$  finish for metallographic analysis. The solid volume fraction was measured manually by point-count method. Typically 3 micrographs were measured to ensure the statistical accuracy of  $\pm 3\ \text{vol.}\%$ . Dihedral angle measurement was performed by manually measuring the angle between two connecting grains using a protractor. The median of 25 observations was reported as the true dihedral angle.

## Experimental Results

All samples achieved nearly full density, except the sample with 90 wt.% W content which achieved only 94% of theoretical density. Solid volume fraction increased as initial tungsten content increased. Distortion decreased as initial tungsten content and solid volume fraction increased. The 80W alloy had the lowest solid volume fraction and most distortion, while the 90W alloy had the highest solid volume fraction and only showed slight distortion.

To investigate the dihedral angle effect on distortion, the solid volume fraction was constant by decreasing the initial tungsten content with decreasing Ni : Cu ratio (As Ni : Cu ratio decreases, W solubility in Ni-Cu matrix decreases). The alloys employed were 80W-16Ni-4Cu (Ni : Cu 8:2), 78.7W-12.8Ni-8.5Cu (Ni : Cu 6:4), 78W-11Ni-11Cu (Ni : Cu 5:5), 77.3W-9.1Ni-13.6Cu (Ni : Cu 4:6), and 75.6W-4.9Ni-19.5Cu (Ni : Cu 2:8). These alloys were liquid phase sintered at  $1480^{\circ}\text{C}$  for 30 min. The heating rate was  $10^{\circ}\text{C}/\text{min}$ . The initial green porosity was 36%, and the pore size was  $87\ \mu\text{m}$ . The measured solid volume fraction was about 0.61 for all the samples. All the samples achieved a sintered density of above 95% of theoretical

density. The sintered density increased slightly as dihedral angle increased, except the 75.6W-4.9Ni-19.5Cu (Ni : Cu 2:8) alloy. Distortion decreased as the dihedral angle increased (Ni : Cu ratio decreased). The sample with dihedral angle of 46 degrees had the most distortion, while the sample with dihedral angle of 76 degrees did not distort.

A comprehensive study of porosity effect on distortion was conducted on three different tungsten alloys, 80W-16Ni-4Cu (Ni : Cu 8:2), 83W-13.6Ni-3.4Cu (Ni : Cu 8:2), and 90W-8Ni-2Cu (Ni : Cu 8:2). Compacts with different green porosities were sintered at 1480°C for 30 min. The heating rate was 10°C/min and the pore size was 87  $\mu\text{m}$ . For the 80W-16Ni-4Cu alloy, all the samples with different green porosities achieved nearly full density and had similar distortion. The distortion parameter for the 80W-16Ni-4Cu alloy is about 0.38. For the 83W-13.6Ni-3.4Cu alloy, all the samples with different green porosities also achieved nearly full density and had similar distortion. The distortion parameter for the 83W-13.6Ni-3.4Cu alloy is about 0.11. The 80W-16Ni-4Cu alloy had more distortion than the 83W-13.6Ni-3.4Cu alloy. Green porosity did not show observable effects on distortion of 80W and 83W alloys after nearly full densification. For the 90W-8Ni-2Cu alloy, samples with green porosities of 37% and 47% achieved nearly full density and showed slight distortion. Sample with green porosity of 57% achieved only 93% density, and sample with green porosity of 67% achieved only 88% density. Both samples retained shape.

All the samples with different pore sizes achieved a sintered density of above 96% of theoretical density, and had similar distortion parameter. Green pore size did not show significant effect on distortion.

For the 80W-16Ni-4Cu alloy, heating rate was adjusted while the green porosity and pore size were held constant. The compacts were heated to 1300°C at 10°C/min, and then the temperature was increased to 1480°C using 1, 3, 5, or 10°C/min heating rates. All of the samples achieved a sintered density above 96% of theoretical density. Distortion decreased as heating rate decreased. The sample with a 10°C/min heating rate had the most distortion, while the sample with a 1°C/min heating rate only showed slight distortion.

The experimental findings show distortion increased with increasing holding time, and distortion did not occur until after nearly full density was achieved. After sintering for 0 min, the compact achieved only 94% density and did not show distortion. After sintering for 2 min, the compact achieved 98.9% density and started to distort. Distortion was significant after sintering for 5 min.

## **Discussion**

In liquid phase sintering, densification and distortion are closely related to liquid content. With high liquid content full density can be achieved even at the particle rearrangement stage [1], but often is the concomitant distortion. With low liquid content the solid skeleton resists densification and also retain the compact shape. This was observed in our experiments. Low tungsten content samples achieved full density and distorted, while the 90W sample only achieved 94% density and did not distort.

Distortion in liquid phase sintering is also associated with low dihedral angles. In low dihedral angles, the reduction in solid-liquid surface energy on first melt formation leads to liquid penetration of grain boundaries [8]. Consequently, densification by rearrangement occurs rapidly and solid-solid bonds do not form before saturation of the intergrain void space [8]. Then the relatively weak capillary force is the only source of strength that disappears as the voids are filled with liquid. Distortion is the consequence

of strength loss, due to loss of solid skeleton strength or capillarity induced strength. Note that full density alloys will distort on reheating to liquid phase sintering temperature, demonstrating liquid attack of grain boundary. On the other hand, high liquid content alloys retain shape up to point of densification or pore closure.

Liquid penetration of grain boundaries leads to compact strength loss. A high solid solubility in the liquid correlates with a low dihedral angle and easy liquid penetration of grain boundaries. The fractional atomic solid solubility in the liquid can be approximately linked to the dihedral angle by the following empirical expression [8]:

$$k_A = 0.11 - 0.14 \frac{\phi}{2} \tan\left(\frac{\phi}{2}\right) \quad (1)$$

where  $k_A$  is the fractional atomic solid solubility in the liquid, and  $\phi$  is the dihedral angle in radians. High solid solubility in the liquid  $k_A$  indicates a low dihedral angle according to Equation 1. The atomic solid solubility in liquid can also be linked to the dihedral angle by the following empirical equation [8]:

$$\phi = 75 - 638\Delta k_A \quad (2)$$

where  $\Delta k_A$  is the fractional atomic solid solubility change in newly formed liquid as compared with the solid solubility in the additive, and  $\phi$  is the dihedral angle in radians. Equation 2 indicates that if the atomic solid solubility in liquid is much larger than the atomic solid solubility in the additive, the systems have low dihedral angles. In turn, low dihedral angles imply easier liquid penetration of the grain boundaries and often distortion.

Solid volume fraction and dihedral angle are the dominant factors controlling densification and distortion during liquid phase sintering [8]. A combination of high solid volume fraction and high dihedral angle results in slow densification without distortion. On the other hand, low solid volume fraction and low dihedral angle result in rapid densification with shape distortion. Such findings allow for mapping probable distortion and densification conditions versus material parameters of dihedral angle and solid content. The data and previous observations [5, 6, 8] with W-Ni-Cu, W-Ni-Fe, W-Ni, W-Cu, Mo-Cu, Mo-Ni, and Fe-Cu agree with the sinter map. We expect this map is also representative for other liquid phase sintering systems with spherical solid grains.

### **Strategies for Distortion Control in Liquid Phase Sintering**

Various strategies emerge to improve distortion control in liquid phase sintering. Since the compact strength evolution determines densification and distortion onset, the design of compositions for densification without distortion requires manipulation of the microstructure and its evolution to sustain compact strength to avoid distortion. As compact strength has contributions from both sinter bonds and capillary forces, in principle, processing strategies that preserve sinter bonds and/or capillary forces will resist distortion. Liquid phase sintering systems that densify slowly resist distortion. These inherently have high solid volume fraction and high dihedral angle. So one option for distortion control is to use high solid volume fraction and high dihedral angle systems. Systems with low solid solubility in liquid inherently have a high dihedral angle and resist distortion. Compositions with presaturated liquid forming agents (for example, prealloy matrix) will inhibit dissolution of sinter bonds into liquid and resist distortion [8]. A slow heating rate at the point of liquid formation allows solid bonds to reform before capillary forces are lost with pore elimination and will resist distortion. Densification and distortion are sequential events during liquid phase sintering; the first focus is on densification. Densification occurs

first. Distortion is inhibited until after nearly full densification when capillary forces are lost and a solid skeleton is not formed. So sintering without full density will also resist distortion.

### **Conclusions**

Solid volume fraction and dihedral angle are the dominant factors on densification and distortion during liquid phase sintering. Distortion decreases with increasing solid volume fraction and dihedral angle. On Earth, green porosity and pore size do not have observable effects on distortion in situation of fast densification where nearly full density is achieved or pores are closed and capillary forces are lost. Quenching results show that distortion is inhibited until pores are closed and the compact is nearly fully densified. Dimensional precision can be achieved by manipulating the microstructure and its evolution to sustain compact strength to avoid distortion in liquid phase sintering. Processing strategies emerge to improve distortion control in liquid phase sintering, including use of high solid volume fraction and high dihedral angle systems, low solid solubility in liquid, compositions with presaturated liquid forming agents, slow heating rate at liquid formation. Densification before full density or pore closure can also prevent distortion.

### **Acknowledgements**

Funding for this research was provided by NASA under grant NAG8-1452, with Mike Purvey as Project Manager.

### **References**

1. R. M. German, *Sintering Theory and Practice*, John Wiley and Sons, Inc., New York, 1996.
2. R. M. German, *Liquid Phase Sintering*, Plenum Press, New York, 1985.
3. W. D. Kingery, *J. Appl. Phys.*, 1959, vol. 30, pp. 301-306.
4. W. D. Kingery and M. D. Narasimhan, *J. Appl. Phys.*, 1959, vol. 30, pp. 307-310.
5. A. Upadhyaya, "A Microstructure-based Model for Shape Distortion during Liquid Phase Sintering," Ph.D. Thesis, The Pennsylvania State University, University Park, PA, 1998.
6. J. L. Johnson, A. Upadhyaya, and R. M. German, *Meta. Mater. Trans.*, 1998, vol. 29B, pp. 857-866.
7. X. Xu, A. Upadhyaya, R. M. German, and R. G. Iacocca, *Inter. J. Refract. Met. Hard Mater.* 1999, vol. 17, pp. 369-379.
8. R. M. German, in *Sintering Science and Technology*, ed. by R. M. German, G. L. Messing, and R. G. Cornwall, Penn State University, State College, PA, 2000, pp. 259-264.
9. W. Yi, "Microstructure Manipulations to Attain Densification without Distortion during Liquid Phase Sintering," Ph.D. Thesis, The Pennsylvania State University, University Park, PA, 2001.